

## PRIORITY DATA

## BACKGROUND OF THE INVENTION

10 FIELD OF THE INVENTION:

15                    This invention further pertains to the separation of inorganic solids, sands, clays, etc., from hydrocarbon compound substrates and mixtures or sludge derived from an originating petroleum source, subsurface or surface, or in the form of petroleum contaminated waste.

This invention also pertains to the complete or partial desulfurization by  
20 reduction of the sulfur-containing species.

This invention also pertains to the remediation of soils by the removal of hydrocarbon contaminants.

**DESCRIPTION OF RELATED ART/PRIOR ART:**

25                   The generally accepted concept of the origination of oil and gas is that it  
was generated from the thermal degradation of kerogen, a fossilized material in shale

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and other sedimentary rock that yields oil upon heating. It is the most common source of carbon in the earth's crust. The major factors affecting the concentration of petroleum are the chemical nature of the kerogen, temperature, time, mineral composition, resident geological structure, etc.

5                   Traditional technology for cracking and hydrogenation, such as catalytically cracking hydrocarbon, serve to form more valuable lower molecular weight products. Hydrocracking reactions between the initial hydrocarbon substrate and the catalytic agent may be carried out in a series of bed reactors or in a distillation column. Such reactions are endothermic and, as such, the reactors must be heated.  
10   Additionally, hydrogen is recycled through the system to ensure maximum hydrocarbon saturation to form the lower molecular weight hydrocarbon products and to remove excess hydrogen generated by the catalytic reaction. In these systems, polyaromatic rings are also opened and the by-products hydrogenated.

                  Substantial quantities of petroleum in the earth have proven difficult or  
15   impossible to recover because they are in the form of high molecular weight hydrocarbon mixtures which are distributed and intermixed in tar sands, shale, and various rock formations. Furthermore, hydrocarbon compounds cannot be economically extracted from "depleted" oil wells because they are not sufficiently concentrated to be extractable by drilling, have lost their original gas pressure, and/or  
20   have relatively high density and viscosity at the given location. The latter compounds will not flow unless heat energy is applied to the petroleum deposit, as, for example, by steam. Additionally, once extracted, these materials still require heat energy to remain as liquids and may be contaminated. Waste or contaminated materials (e.g., soil, rock, sludge, oil tars) containing hydrocarbons, crude or refined, cannot be economically  
25   extracted from naturally or man-made contaminated materials.

                  There are well known enhanced production techniques to obtain oil from depleted or under-producing wells. *In situ* combustion is a technique used to heat crude petroleum materials below the surface of the earth to reduce their viscosity. An oxidizing agent, such as air, is injected into the subsurface deposit at sufficiently high  
30   temperatures to initiate a combustion process or a phosphorous bomb or gas burner is

lowered into the well. The lower molecular weight hydrocarbons generated then rise to the surface of the deposit. There are drawbacks to this procedure in that the high temperatures necessary for combustion, combined with the presence of oxygen, lead to undesirable side reactions of coking and the formation of phenols and ketones, which are difficult to process through other refining techniques.

Thermal recovery techniques from under-producing, depleted, and heavy oil wells and bitumen deposits may also comprise steam injection. The purpose of the injected steam is to heat the heavy hydrocarbon deposit, thereby significantly reducing the viscosity and making an economically acceptable level of recovery of the hydrocarbon deposit. *In situ* hydrovisbreaking and steam flooding are alternatives to the combusive techniques. Sometimes, in this process, a catalyst is suspended in the steam and circulated throughout a subsurface deposit. This heat permits the endothermic reaction to occur, causing lower molecular weight hydrocarbons rise to the surface of the petroleum deposit. This process may only be used in formations that have sufficient overburden thicknesses to withstand the injection of high temperature, high pressure materials.

Waterflooding techniques are also a frequently employed method to improve oil recovery from depleted or nearly depleted oil wells and can be expected to yield between 5% and 50% of the remaining petroleum products. The water to be injected must first be filtered to eliminate all potentially reactive particles. Then it is pumped into the well under pressure either from a group of strategically placed injection wells or from injection wells at the edge of the oilfield. Water rarely circulates evenly through the underground deposits. In most cases, the water permeates the deposits until it causes a breakthrough, creating a path of least resistance to the producing well along which the water will flow. The oil has a lower specific gravity than water and floats on top of the water. Such waterfloods are most effective in areas where there is little primary production. Variants of this technique include alkaline or caustic flooding, which involve the addition of basic agents to the water, such as sodium hydroxide.

Miscible gas drive for enhanced oil recovery involves injecting an inert gas, such as carbon dioxide, nitrogen, or liquefied petroleum gas into the reservoir. The gas mixes with the petroleum deposits, making the oil less viscous, and pressures the fluid oil towards the producing well. Sometimes alternating between pumping gas and water through the well is employed. Solvent or chemical flooding comprises injecting a liquid with different chemicals in batches (slugs) into a deposit. A micellar-polymer flood will contain a polymeric surfactant to wash reservoir pore spaces clean of the heavy oils present within the earth formation. Other solvents can be used to mix with and reduce the viscosity of the petroleum deposits. Frequently used solvents include aromatic hydrocarbons, carbon disulfide, and carbon tetrafluoride, which are all capable of dissolving bituminous petroleum deposits. Water-based solvents have been used, with both heated and unheated water, to carry active ingredients throughout subsurface formations. Solvents or chemicals are frequently pumped through pipelines along with the treated oil. These must be separated out, e.g., by distillation to preserve both expensive solvents and the treated oil. Elimination of this refining step would reduce complications and cost.

It can be relatively difficult and economically unfeasible to separate hydrocarbon compound mixtures from some of the inorganic solid materials that are naturally intermixed.

#### BRIEF SUMMARY OF THE INVENTION:

This invention relates to compositions and methods for cracking and hydrogenating high molecular weight hydrocarbons to produce lower molecular weight hydrocarbons from substrates containing relatively higher molecular weight hydrocarbons. Hydrogenation is facilitated by the presence of water and, optionally, by the addition of refined and unrefined alkane and cycloalkane hydrocarbons (C<sub>5</sub>-C<sub>25</sub>). The treatment with the inventive composition results in the lower molecular weight characteristics, as can be shown by both increased API value (generally the API value





clinopyroxene. Pyroclastic rock is rock which is formed by either a volcanic explosion or an aerial expulsion from a volcanic vent. Volcanic glasses are called obsidian and consist of silica particles fused by the intense heat of a volcano. Basalt is a mafic, igneous rock composed of plagioclase. Different varieties of basalt differ in their degree of silica saturation. Zeolites are a family of aluminum silicate minerals that may occur naturally or be produced synthetically. Zeolites from British Columbia typically consist of about 89%  $\text{SiO}_2$ , 0.8%  $\text{Fe}_2\text{O}_3$ , and about 1%  $\text{CaO}$ .

Any transition metal salt with a +2 or +3 oxidation state will function in the catalytic composition. Preferred compounds include ferric chloride, ferrous chloride, cupric chloride, and cobalt chloride. Ferric chloride is the most preferred.

Not including the specific metal oxides listed above, the most preferred metal oxide is titanium dioxide ( $\text{TiO}_2$ ). In the most preferred embodiment, titanium dioxide accounts for about 2% by weight of the total weight of the catalytic composition. Boron oxide ( $\text{B}_2\text{O}_3$ ) can also be substituted and used in place of and in concert with  $\text{TiO}_2$ .

The components other than Portland cement are varied depending on the specific high molecular weight substrate being treated. Such customization can be readily carried out by testing small samples of the substrate with different catalytic compositions to determine the most effective components and relative component ratios. Particular examples are set forth below. Solid components may account for 2-10% by weight of the catalytic composition, and preferably comprise 5-10% by weight.

Though specific materials are recited herein by their common names, it will be understood that other composites formed of various minerals and compounds may also be used.

Optionally, refined and unrefined alkanes and cycloalkanes, such as naphtha or diesel fuel, of the C<sub>5</sub> to C<sub>25</sub> range are frequently employed to facilitate and intensify the hydrogenation process. This refined or unrefined hydrocarbon component is incorporated to serve as a hydrogen donor. The included water will also function as a hydrogen source. Typically, diesel fuel or naphtha is mixed with the high molecular weight hydrocarbon substrate prior to the addition of the aqueous colloid suspension.

The refined or unrefined hydrocarbon component may consist of any C<sub>5</sub> to C<sub>25</sub> alkane or cycloalkane or mixture thereof and may range from 0 to 50% by weight of the total catalytic composition added. Naphtha or condensate is the most preferred refined hydrocarbon.

5                   Catalytic composition to crude oil loading may vary from a ratio of 2:1 to 4:1. The preferable loading ratio is 3:1.

After vigorously admixing the catalytic composition in water with the high molecular weight hydrocarbon compounds and, optionally, with a refined hydrocarbon at ambient temperatures and pressures, a rapid, almost instantaneous, reaction of cracking and hydrogenation occurs to produce a product composed of lower molecular weight hydrocarbons. The lower molecular weight hydrocarbons float on top of the water-based colloid in a separate layer. Sulfur-based and metallic impurities form solid, inert precipitates upon reaction with the catalytic composition after mixing. The process proceeds to completion very rapidly, often within minutes from the time of complete addition of the catalytic composition with no CO<sub>2</sub> or CO emissions.

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The terms high molecular weight hydrocarbon and low molecular weight hydrocarbon as used herein are relative terms to one another. The term high molecular weight hydrocarbon signifies a mixture of hydrocarbons and their entrained impurities with an average molecular weight of the hydrocarbons higher than the average molecular weight of the hydrocarbons in a low molecular weight hydrocarbon. Thus, the use of the terms "high molecular weight hydrocarbon" and "low molecular weight hydrocarbon" does not signify any particular molecular weight ranges.

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High molecular weight hydrocarbons are typically materials such as crude oils, asphaltenes, tars, heavy oils, and the like which have limited or no practical use, but which can be converted to more valuable and useful lower molecular weight hydrocarbons via chemical means. Medium oils have resins or polar fractions less than about 25% of the weight of the total oil and have API gravity of 20 to 30 with viscosities in the range of about 100 to 1000 centipoise; heavy oils have resins or polar fractions between about 25 and 40% of the total weight of the oil and have API gravity of 10 to 20 with a viscosities in the range of about 100 to 10000 centipoise; tars have

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resins or polar fractions greater than about 40% of the total weight of the oil and have API gravity less than about 8 to 10 and a viscosity greater than about 8000 centipoise.

The lowest molecular weight hydrocarbons may include C<sub>1</sub> to C<sub>4</sub> gases, e.g., methane, propane, natural gas. The inventive process also results in a reduction of density and viscosity and an increased API gravity value in the treated hydrocarbon mixture.

In the inventive process, any solid fraction in the starting high molecular weight hydrocarbon (soils, sediments, rock mixtures, sands, etc.) will precipitate to the bottom of the aqueous mixture. A significant percentage of heavy metal ion impurities in the starting high molecular weight hydrocarbon will attach or bind to the solid fraction in the precipitate. The low molecular weight hydrocarbon product will float to the surface of the water allowing for easy retrieval of the products.

## 1. SUBSURFACE APPLICATION

For treatment of a high molecular weight hydrocarbon below the earth's surface, the solids in the inventive catalytic composition are initially slurried with water or with a water/refined hydrocarbon mixture. This mixture is then injected into a reservoir or source rock formation of an oil or gas well. This petroleum-containing geologic formation associated with a given oil and/or gas well may be considered "dead" or under-producing and still be a candidate for the inventive treatment. The catalytic composition will reduce oil density, increase API gravity, and reduce the viscosity of any contacted oil deposits. This will increase the value of the oil per barrel. Typical barrel price of heavy oil, with an API below 16, is about \$8 to about \$10. With the addition of about \$1.50 to \$2.00 of chemistry per barrel, the value of the same oil will increase to about \$15 to about \$18 per barrel.

In the context of a fracture and/or stimulation project on the given well, the composition may be injected under pressure. The chosen catalytic composition is directed to the reservoir formation associated with the oil or gas producing formation which has been deemed to have the greatest amount of oil and gas. The catalytic



substrate of high molecular weight hydrocarbon material. Diesel fuel or condensate or a like refined or unrefined hydrocarbon is added to the admixture as a supplemental hydrogen source for the cracking reactions. Upgrading consists of chemically treating or fractionating bitumen or heavy oils to increase its value by reducing the density and viscosity, thereby generating a higher quality crude oil substitute. The specific objectives of upgrading are to increase the percentage of the saturate and aromatic fractions, reduce the polar and pentane insoluble fractions, reduce viscosity, increase API gravity, and reduce overall hydrocarbon molecular weight. API gravity is a term to relate the relative specific densities of oil products developed by the American Petroleum Institute. To convert between API gravity and specific gravity, the following formula should be followed: API to specific gravity:  $SG = 141.5/(131.5 + ^\circ\text{API})$ .

By reducing the density, increasing the API gravity, and reducing the viscosity heavy oil or tar sands bitumen would need no or reduced addition of condensate to allow the oil to be pumped through pipes. For example, there exists a pipeline that moves 778,000 barrels of heavy oil per day from Alberta to U.S. In addition to the oil, 300,000 barrels of condensate are added so it can be pumped. The value of the oil is currently \$12 per barrel. If the API gravity were 20 to 23, then there would be no need of condensate. The value of the treated oil would now be \$16-\$18 per barrel and the operator could then pump 1,000,000 barrels of oil per day. Condensate is in such short supply that the condensate is currently distilled out of the oil in the U.S. and pumped back to Alberta daily.

For surface applications of the present invention, the inventive reaction may be carried out at ambient temperatures and pressure, i.e., at about room temperature, which is defined as about 20 to 25°C (about 68 to 77°F). Ambient pressure is about 1 atmosphere (about 760 Torr).

### 3. DESULFURIZATION AND THE ELIMINATION OF HYDROGEN SULFIDE

Hydrogen sulfide may be generated in large amounts by thermal cracking from kerogen and from liquid sulfur-containing compounds present in crude oils. Sulfur content of crude oil generally decreases with depth, possibly due to cracking and elimination of sulfur as  $H_2S$ . The total sulfur content in crude oil, heavy oil, bitumens, and tars varies from 0.04% to 8%. Generally, oils with high densities and low API gravities will have higher sulfur contents.

Some of the hydrogen generated from surface catalytic reactions between the catalytic composition and water and with the refined or unrefined hydrogen source will convert sulfur heteroatoms in the polar (resin) and asphaltene fractions to  $H_2S$ . Through a series of oxidation reactions, the catalytic composition converts the  $H_2S$  to  $CaSO_4$ . Free sulfur, if present, may also react with the hydrocarbons to produce  $H_2S$ . Sulfate reduction, if present in the sediments, and the related oxidation of hydrocarbons may also occur beyond  $150^\circ C$ , resulting in the generation of  $H_2S$  and  $CO_2$ .

### 4. SOIL DECONTAMINATION

The inventive catalytic compound may be mixed with contaminated soil in a tank containing water and mechanically agitated with the injection of air. The contaminated soil will be remediated through the cracking and hydrogenating the impurities. The treated soil will precipitate to the bottom of the reaction vessel and the organic waste products will float on the surface of the water. The hydrocarbon layer can be decanted off and reused as a secondary fuel. Also, the catalytic compound may be injected and mixed into the soil on the ground, achieving the same end state results.

The following examples illustrate embodiments of the invention, but are not intended to be limiting:

Example 1:

Crude oil samples (about 200 to 250 grams each) were taken straight from the well at the Lloydminster oil fields, Lloydminster, Alberta, Canada (API gravity 16 to 18) and Peace River oil fields, Peace River, Alberta, Canada (API gravity 8 to 10). The samples were each placed in two-liter jars and an equal weight of water heated to 100°C was added to facilitate mixing with the catalytic composition. The samples were allowed to cool to ambient temperature (16°C) after treatment. The jars had screw-on gas tight lids with rubber diaphragms in place of a hole that had been drilled in the covers to allow withdrawal of headspace gas samples for analysis. The inventive composition, in powder form, was added to each of the samples in amounts of 5 and 10% by weight to weight of oil. The composition contained 48% Portland cement, 42% volcanic glasses-red scoria, 8% ferric chloride and 2% titanium dioxide, all percentages being based on the total weight of the composition.

The following table shows the weight percent of Portland cement and volcanic ash components in the catalytic composition.

**TABLE 3:**

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO
<b>Catalytic Composition</b>				
<b>Portland Cement</b>	8.65%	2.10%	1.30%	27.03%
<b>Volcanic Ash</b>	34.65%	3.97%	1.03%	0.12%

The samples were then stirred with a metal rod for 1.5 to 2 minutes and the lids were then screwed on tightly. A separate set of control samples of each crude oil without the added catalytic composition were allowed to stand for four days at ambient temperatures and pressure. Thereafter, the headspace gases were analyzed by gas chromatography for each sample.

Significant amounts of hydrocarbon gases were found in the headspace gas of the Lloydminster samples, except for the control, in which there was only a

water and oil mixture present. Specifically, compared to the control sample, the treated headspace gas contained 41 times more methane, 23 times more ethane, 14 times more propane, 10 times more isobutene, and 71 times more butane. The speed of the reaction is very fast and that for the Peace River samples, hydrocarbon gases were generated very rapidly and lost before the lid could be placed on the jar, or not generated for some reason. The composition of the headspace gases was determined by gas chromatography.

Additional tests with crude oil from Lloydminster field showed that hydrocarbon gases were rapidly generated and the analysis indicated that 2 to 3% of the total initial carbon was converted to C<sub>1</sub> to C<sub>4</sub> hydrocarbon gases, with methane being the most prominent in quantity. No hydrocarbon gases were found in the headspace gases of the treated Peace River samples.

Saturate, aromatic, polar, and pentane insoluble fractions (SAPA) analysis of the treated and untreated heavy oil showed significant changes in the Lloydminster heavy crude oil samples. The 9% and 8% increases in the saturates and aromatic fractions, respectively, and the 19% and 1% decreases in the polar and pentane insoluble fractions, respectively, represent significant improvements in the quality of that heavy oil sample.

There was a consistent 2% lower distillation temperature across the mass spectrum of the saturates fraction for the untreated Lloydminster heavy oil relative to the saturates fraction of the untreated oil. This means the treated saturates fraction was a relatively lighter molecular weight fraction than the untreated saturates fraction.

### Example 2:

Samples of Syncrude bitumen were prepared to demonstrate the effectiveness of different embodiments of the present invention. Three liquid samples of Syncrude bitumen were blended with 35-50% by weight of naphtha. For two samples, the catalytic composition was prepared by adding the inorganic composition to hot tap water and mixing with a metal stirring rod the resulting colloid into the crude

oil sample. The third sample received no addition of the catalytic composition and serves as the control. The catalytic composition called "Mix 1" consisted of 45% by weight Portland cement, 45% by weight volcanic scoria from British Columbia, 2% by weight titanium dioxide, and 8% by weight ferric chloride. "Mix 2" consisted of 45% Portland cement, 45% clinoptilolite zeolite from British Columbia, 2% titanium dioxide, and 8% ferric chloride.

The following table shows the weight percent of the Portland cement and volcanic ash components in the Mix 1 and Mix 2 catalyst compositions.

**TABLE 4:**

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO
<b>Catalytic Compositions</b>				
<b>Mix 1</b>				
<b>Portland Cement</b>	8.65 %	2.10 %	1.30 %	27.03 %
<b>Volcanic Ash</b>	20.70 %	0 %	8.10 %	0 %
<b>Mix 2</b>				
<b>Portland Cement</b>	8.65 %	2.10 %	1.30 %	27.03 %
<b>Zeolite</b>	40.05 %	0 %	0.36 %	0.45 %

100 grams of naphtha were added to 300 grams of hot tap water and 10 grams of the catalytic compositions described above, for those samples receiving the composition.

The inventive treatment for each oil sample was added and mixed vigorously for about 30 seconds. The reaction was completed almost instantaneously. The liquid in the jar separated into three layers; the treated oil at the top, a water layer in the middle, and a precipitate of inorganic material at the bottom. The gas generation occurred slowly through low bubbling and was even evidenced briefly in the sample without the catalytic composition.

When the reaction vessels were opened, measurements were conducted to determine the change in the viscosity of each sample and SAPA (Saturate, Aromatic,

Polars or resins, and Pentane insolubles or asphaltenes) analyses were performed.

Table 5 below uses these characteristics to demonstrate the properties of each sample.

**TABLE 5:**

<b>Oil Sample</b>	<b>Saturates</b>	<b>Aromatics</b>	<b>Polars or Resins</b>	<b>Pentane Insolubles – Asphaltenes</b>	<b>API</b>	<b>Viscosity (centipoises)</b>
Syncrude Bitumen & Naphtha – Untreated	12	26.4	40.7	20.9	27.3	91.88
Syncrude Bitumen, Naphtha, & Mix 1	13.8	23.9	37.4	24.9		91.88
% Change	+15.0%	-9.5%	-8.1%	+19.1%		
Syncrude Bitumen, Naphtha & Mix 2	13.1	22.4	41.8	22.7		380.8
% Change	+9.2%	-15.2%	+2.7 %	+8.6%		

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After 24 hours, headspace gases generated in each sample were analyzed. The gas analyses of the Mix 1 and Mix 2 samples showed the same compounds and relative concentrations as was found in the untreated control sample. However, the CO<sub>2</sub> level was 91% less in the treated samples than it was in the untreated sample. It is possible that the hydrocarbon gases generated by the inventive process were reabsorbed into the treated hydrocarbon mass.

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### Example 3:

Samples of heavy oil from the Lloydminster oil fields were prepared to demonstrate the effectiveness of different embodiments of the present invention. This sample had an initially high polar fraction, 38.7%. Polar fractions have a dramatic effect on the viscosity and density of an oil sample. Two 200-gram liquid samples of

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oil bitumen with an initial API gravity of 9.9 were tested. The process for addition and composition of the catalytic composition used in this example is the same as that described in mix 1 of example 2 above. The specific catalytic composition consisted of 45% by weight Portland cement, 45% by weight volcanic scoria from British Columbia, 2% by weight titanium dioxide, and 8% by weight ferric chloride.. Diesel fuel and the catalytic composition were added to Sample 1. After 1 hour, the API gravity of Sample 1 had reached 22.1 and, after 24 hours, was 27.3. Sample 2 had no diesel fuel added, and reached an API gravity of 14.9 one hour after the addition of the catalytic composition, and an API gravity of 17.5 24 hours later.

After 24 hours of reacting, the reaction vessels were opened and measurements were conducted to determine the change in the viscosity of each sample and SAPA (Saturate, Aromatic, Polars or resins, and Pentane insolubles or asphaltenes) analyses were performed. Table 6 below uses these characteristics to demonstrate the properties of each sample.

**TABLE 6:**

<b>Oil Sample</b>	<b>Saturates</b>	<b>Aromatics</b>	<b>Polars or Resins</b>	<b>Pentane Insolubles - Asphaltenes</b>	<b>API</b>
Untreated Oil	17	25	22.0	19	9.9
Sample 1	21	25	22.0	14	27.3
% Change	+24 %	0	0	-26 %	176 %
Sample 2	20	26	18	17	17.5
% Change	+18 %	+4 %	-18 %	-11 %	77 %